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(19) (CA) **APPLICATION FOR CANADIAN PATENT** (12)

(54) Method for Preventing Hydrates

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Canada

ABSTRACT

A METHOD FOR PREVENTING HYDRATES

The invention relates to a method for preventing or retarding the formation of hydrates or for reducing the tendency of hydrates to agglomerate in a stream of fluid comprising water and hydrocarbon during transport of the fluid through a conduit, which method comprises adding to the fluid an alkyl aryl sulphonic acid or an alkali metal- or ammonium salt thereof substantially in the absence of glycol flowing in the stream.

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A METHOD FOR PREVENTING HYDRATES

The invention relates to a method for preventing or retarding the formation of hydrates or for reducing the tendency of hydrates to agglomerate during the transport of a fluid through a conduit.

It is well known in the art that the formation of hydrates in a conduit, e.g. a pipeline, during the transport of oil and gas can be a serious problem, especially in areas with a low temperature in the winter season or in the sea. Generally the temperatures are so low that hydrate formation, due to the inevitable presence of coproduced water in the wells, takes place if no special steps are taken. It is possible to insulate a pipeline when during transport from the well, the temperature of the fluid in the pipeline decreases. Insulation decreases the chance of hydrate formation, but on the other hand it is expensive. If the field is relatively small and at long distance from the production platform the costs of insulation may be too high to make the field economically attractive.

It is also known to control the hydrate formation by addition of chemical compounds in the fluid which is transported, e.g. by the use of glycols, e.g. ethylene glycol or diethylene glycol. A disadvantage thereof is that large amounts of glycol are needed (in the order of 30% by weight calculated on the amount of water).

In the U.S.S.R. Inventor's Certificate 697696 is disclosed a composition suitable for the prevention of hydrate formation, which composition comprises diethylene glycol with a minor amount of alkyl aryl sulphonate (in a quantity of 0.3-0.5% based on the weight of the diethylene glycol).

Surprisingly it has been found that alkyl aryl sulphonic acids or alkali metal- or ammonium salts thereof can be used without glycols, to control hydrate formation.

The invention relates to a method for preventing or retarding the formation of hydrates or for reducing the tendency of hydrates to agglomerate in a stream of fluid comprising water and hydrocarbon during transport of the fluid through a conduit, which method comprises adding to the fluid an alkyl aryl sulphonic acid or an alkali metal- or ammonium salt thereof substantially in the absence of glycol flowing in the stream.

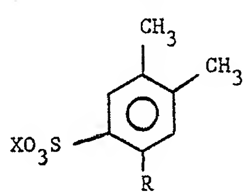
The hydrocarbon may be a liquid or a gas, but is preferably a gas such as methane, ethane, propane, isopropane, butane or isobutane. The fluid may be produced from oil wells as well as from gas wells. The fluid may also include natural gas.

Depending upon the pressure hydrates may be formed at temperatures well above the freezing point of water. Ethane hydrates, for example, are formed at pressures between 10 and 30 bar (1 and 3 MPa) and temperatures between 4 °C and 14 °C. Formation and agglomeration of hydrate crystals will thus easily occur in pipelines surrounded by a cold atmosphere.

The problem of formation and agglomeration of gas hydrates is not limited to gas wells, but also occurs in oil wells, if water and gas are present in the fluid.

The alkyl aryl sulphonic acids or their salts preferably have an aryl group derived from benzene, toluene, ortho-, meta- or para-xylene. The alkyl group is preferably a long chain alkyl group, which may be branched or straight. The alkyl group may be e.g. a C_8-C_{22}-alkyl group.

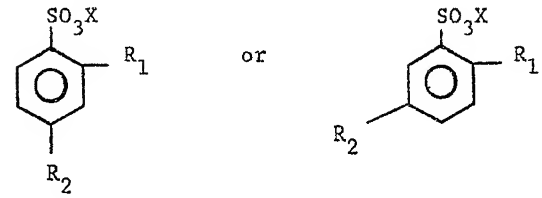
Preferred compounds are those of the chemical formula



wherein X is H, Na or K and R is a C_8-C_{22} alkyl group.

More preferred compounds are those wherein R is a C_{13} and/or C_{14} alkyl or a C_{18}-alkyl group, such as those known under the trade name DOBANAX-320, DOBANAX-313 and DOBANAX-205.

Other groups of preferred compounds are dialkyl benzene sulphonates of the chemical structure



wherein X is an alkali metal and R_1 and R_2 are the same or different C_2-C_{20}-alkyl groups, preferably C_6-C_{14}-alkyl groups.

The alkyl aryl sulphonates are added in quantities from 0.1 per cent to 3 per cent by weight, calculated on the weight of the water present in the fluid. A preferred range is from 0.2 to 1 percent, more preferred in the range of from 0.3 to 0.6 per cent.

To study the influence of a small quantity of alkyl aryl sulphonates on the nucleation temperature, kinetics of the crystal growth and morphology of the crystals, a high pressure, jacketed visual cell was built. The cell was made of stainless steel and had a cooling jacket to allow a good and easy temperature control of the cell. Two sapphire windows allowed visual observation of the cell content. The cell was provided with two valves one for the introduction of liquid and one for gas. At the bottom of the cell a stirring bar cared for good mixing of the cell content. The inner volume of the cell was 66.4 ml and dead volumes were reduced to a minimum. The cell was further tested together with its loading system at a pressure of 100 bar over a period of 80 hours without any pressure drop being observed. The cell usually worked at a pressure of below 30 bar. The cell was located in a plexiglass cage.

A personal computer based data acquisition system allowed the measurement of the temperature and pressure inside the cell once per minute. The set point of a thermostated bath, connected to the cooling jacket, could be set automatically by the computer. A steel well went deeply inside the cell in which a platinum resistance thermometer was introduced. On the cell was mounted a pressure

transducer, with a very small temperature hysteresis and a high accuracy.

Before a run was made, the cell was rinsed with demineralized water, rinsed with ethanol and vacuum dried, all without dismounting the cell.

To carry out the experiment demineralized water and decane were introduced as liquid into the cell. The water contained 0.5% per cent by weight of alkyl aryl sulphonic acid or salt thereof, if desired. Ethane was introduced as a gas into the cell. The run started at 20 °C and the temperature in the cell was dropped, via the jacket connected to the thermostatic bath by lowering its temperature. The amounts of water, decane and ethane were 25, 5.8 and 4.7 grams respectively. The pressure was 25 bar at 20 °C, and no ethane hydrates were formed.

The thermometer sent a digital signal, the pressure meter an analog signal, to the computer. The computer could also send a set point command to the thermostatic bath. During each experiment the temperature and the pressure of the cell were recorded, together with the time, at every minute. Of a given composition, comprising water, decane and ethane and if desired the alkyl aryl sulphonic acid or salt thereof, a temperature-time and a pressure-time curve could be made.

By lowering the temperature, which was accompanied by a pressure drop, to below the equilibrium temperature point at which hydrates and liquid were in equilibrium, ethane hydrates were formed. The rather sudden formation of hydrates was read from the temperature- and pressure-time curve. A relatively steep rise in temperature (about 0.5 °C) and a pressure drop (about 1 to 5 bar) occurred.

At the same time the formation of hydrates was seen through a sapphire window. The formation of hydrate crystals consumes the free ethane molecules. The progressive drop of the cell pressure that occurs after nucleation has started is a good indication of the quantity of hydrate formed as a function of time.

It was further observed that in the hydrate formation the crystals agglomerated in case that alkyl aryl sulphonate was not added.

In the method according to the invention, however, the addition of an alkyl aryl sulphonate prevented the formation of agglomerates of hydrates.

EXAMPLE 1

25 g of water, 5.8 g of decane, 4.7 g of ethane and 0.5% by weight, based on the water, of di-linear C_8-C_{10}-alkyl benzene sulphonate (sodium salt), were used as described above in the cell. The experiment started at 20 °C and after lowering the temperature to 8.4 °C crystallization occurred, while at the same time the pressure in the cell decreased from 22 bar to 13 bar. No agglomeration of the hydrate was observed.

EXAMPLE 2

25 g of water, 5.8 g of decane, 4.7 g of ethane and 0.5% by weight, based on the water, of sulphonated "SOMIL SH" (SOMIL is a Trade Mark) were used as described above in the cell. The experiment started at 20 °C and after lowering the temperature to 8.4 °C crystallization occurred, while at the same time the pressure in the cell decreased from 22 bar to 16 bar. No agglomeration of the hydrate was observed.

EXAMPLE 3

25 g of water, 5.8 g of decane, 4.7 g of ethane and 0.5% by weight, based on the water, of C_{18}-alkyl benzene sulphonic acid were used as described above in the cell. The experiment started at 20 °C and after lowering the temperature to 8.4 °C crystallization occurred while at the same time the pressure in the cell dropped from 22 bar to 16 bar. No agglomeration of the hydrate was observed.

Comparative Example A

25 g of water, 5.8 g of decane and 4.7 g of ethane were used as described above in the cell. Also in this case the experiment started at 20 °C and after lowering the temperature to 9.4 °C crystallization occurred and was followed by agglomeration of the crystals.

C L A I M S

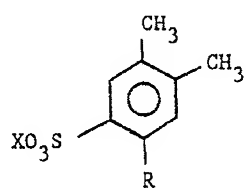
1. A method for preventing or retarding the formation of hydrates or for reducing the tendency of hydrates to agglomerate in a stream of fluid comprising water and hydrocarbon during transport of the fluid through a conduit, which method comprises adding to the fluid an alkyl aryl sulphonic acid or an alkali metal- or ammonium salt thereof substantially in the absence of glycol flowing in the stream.

2. A method as claimed in claim 1 wherein the fluid comprises one or more hydrocarbons consisting of the group: methane, ethane, propane, isopropane, butane and isobutane.

3. A method as claimed in claim 1 or 2 wherein the fluid comprises natural gas.

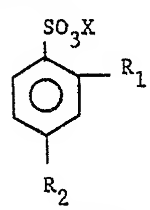
4. A method as claimed in one or more of the claims 1-3 wherein is added to the fluid a C_8-C_{22}-alkyl aryl sulphonic acid or an alkali metal- or ammonium salt thereof.

5. A method as claimed in claim 4 wherein a compound of the chemical structure

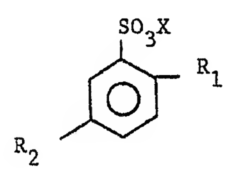


wherein X is H, Na or K and R is a C_8-C_{22} alkyl group, is used.

6. A method as claimed in claim 1 wherein a compound of the chemical structure



and/or



wherein X is an alkali metal and R_1 and R_2 are the same or

different C_2-C_{20}-alkyl groups, preferably C_6-C_{14}-alkyl groups, is used.

7. A method as claimed in one or more of the claims 1-6 wherein the quantity of alkyl aryl sulphonate ranges from 0.1 per cent to 3 per cent by weight, calculated on the weight of the water present in the fluid.

8. A method as claimed in claim 7 wherein the quantity of alkyl aryl sulphonate lies in the range of from 0.2 to 1 per cent.

9. A method as claimed in one or more of the claims 1-8 characterized by the substantial absence of a glycol.

10. A method for preventing or retarding the formation of hydrates on for reducing the tendency of hydrates to agglomerate as claimed in claim 1 as hereinbefore described with special reference to the Examples 1-3.

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